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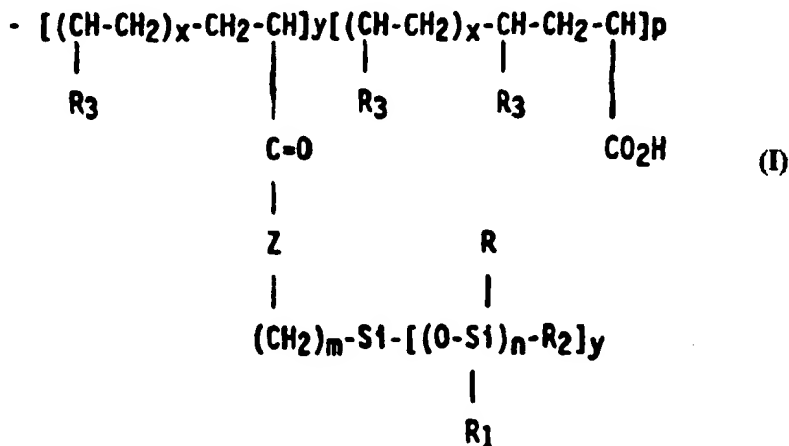
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(54) Title: SILOXANE MODIFIED POLYOLEFIN COPOLYMERS

(57) Abstract

A siloxane modified copolymer with general formula (I), wherein: $x = 1$ to 1,000; $m = 2$ to 100; $n = 0$ to 1,000; $y = 1$ to 3; and $p = 1$ to 200; wherein R and R_1 are independently selected from the group consisting of hydrogen, alkyl groups having 1 to 6 carbons, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R_2 is selected from the group consisting of C_1 to C_6 alkyl, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R_3 is methyl, ethyl or propyl; and

Z is O, S, NH or NR' wherein R' is phenyl, C_1 to C_4 alkyl or C_1 to C_3 alkylphenyl is prepared by the following process: reactively extruding organosiloxanes having reactive terminal groups with polyolefins having reactive groups, the molar ratio of the functional groups being from about 1:1 to about 1:100,000 in a substantially solvent-free environment at a temperature from about 150 °C to about 350 °C for not more than 1 hour at 50 to 350 rpm.



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SILOXANE MODIFIED POLYOLEFIN COPOLYMERS

TECHNICAL FIELD

This invention relates to siloxane modified polyolefin copolymers and a process for making them. The copolymers are used to make dispensing films and plastics for packaging, measuring, and adhesive releasing objects.

BACKGROUND

Siloxane modified polyolefin copolymers have been long known in the art and have various industrial applications. They retain the favorable characteristics of both polysiloxanes and polyolefins. Polysiloxanes are known for their thermostability, chemical stability, low surface energy, and lubricating properties. Poly- α -olefins are chemically stable, have high resistance against physical force, and molding or shaping capability. The α -olefin polymers are usually mixed with other hydrocarbon polymers such as polyethylene and polypropylene. Mixing siloxane polymers with α -olefin polymers leads to leaching; i.e., one polymer forms a layer or film on the other polymer.

Siloxane modified polyolefin copolymers were developed for use as electrical insulating material and as substitutes for polyethylene. The siloxane modified polyolefin copolymers are synthesized by reacting low molecular weight polyolefins with cyclosiloxanes in the presence of catalysts such as Ziegler-Natta catalysts, peroxides and other free radical initiators and at temperatures from 100° to 200°C. These copolymers were also made by melt mixing polyolefins and olefin substituted siloxanes. These products are both graft copolymers and block copolymers.

Another way of combining hydrocarbons and siloxanes is by reacting functional groups attached to each of the oligomers, macromers, polymers or monomers. Carboxylic acids or anhydrides can link with hydroxyl groups to form esters, primary and secondary amines to form amides or

imides, primary amines to form imides and tertiary amines to form quaternary amine salts. The amides, imides and esters are more stable than the quaternary ammonium salts. As is to be expected, the ionic link of the quaternary salt hydrolyzes on standing. The chemical bonds found in the esters, imides and amides appear to be quite stable during use.

There have been problems producing chemically bonded siloxane and polyalkyl copolymers. If there is more than one functional group on the silicone oligomer, the product may be unacceptable. Subsequent processing into thin structures, e.g. extruding or co-extruding the material into films or sheets, becomes difficult.

It has now been found that by reacting functional derivatives of siloxanes with substantially one reactive group per molecule and polyolefins polymers containing one or more functional groups, copolymers containing the siloxane functionality and polyethylene or other polyalkyl functionality can be obtained. The oligomers are reacted at defined ratios and under specific temperature and mixing conditions in an extruder. Some difunctional or multifunctional groups can be present. The level of these difunctional or multifunctional groups determines the level of cross linking in the final product. Cross linking can cause problems when forming copolymers into thin films, sheets or bottles. Preferably, monofunctional silicone reactants are used. The copolymers obtained by this method can be mixed directly with other polymers or coextruded with other polymers into multilayer structures, including sheets, films or bottles.

Silicone containing copolymers have a tendency to migrate to the surface of films and plastics. The mixed copolymers made herein acquire surface characteristics of the silicone polymer, but have the advantage that the siloxane is chemically linked to another polymer. Thus the siloxane does not separate or leach out of the film or package as the physical mixtures can. The films and

plastics obtained by this invention are particularly useful in packaging, for measuring and dispensing devices, and adhesive releasing materials. They are particularly useful for making bottles for low surface energy liquids.

5 It is an object of the present invention to provide copolymers which have the favorable characteristics of both polysiloxanes and polyolefins, but are thermoplastic, heat-sealable and more stable than mixtures of the polymers.

10 It is also an object of the present invention to provide a practical and efficient process to obtain a siloxane modified polyolefin. The process does not require a solvent and therefore is environmentally sound and more economical to run.

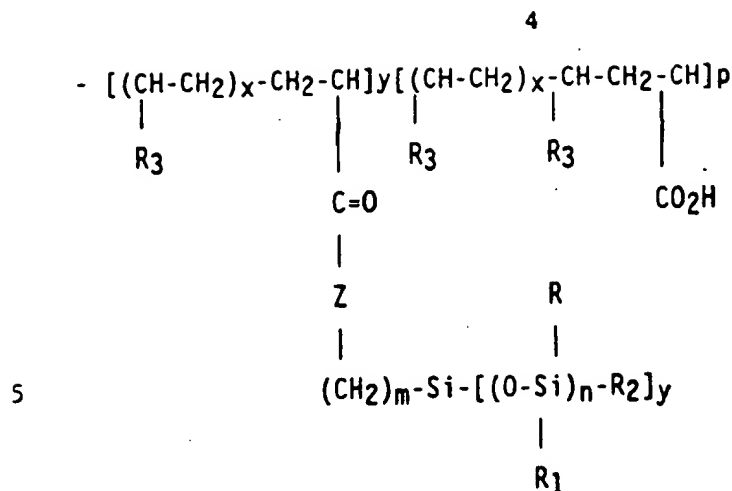
15 It is further an object of the present invention to provide a convenient method of using these siloxane modified polyolefins with other polymers to make films and other plastic articles.

SUMMARY OF THE INVENTION

20 A process for obtaining siloxane modified polyolefin copolymers comprising:

Reactively extruding organosiloxanes having reactive terminal groups with polyolefins having reactive groups, the molar ratio of the functional groups being from about
25 1:1 to about 1:100,000 in a substantially solvent-free environment at a temperature from about 150°C to about 350°C for not more than 1 hour at 50 to 350 rpm is disclosed.

The resultant copolymer has the following general
30 formula:



wherein:

$x = 1$ to 1000

$m = 2$ to 100

10 $n = 0$ to 1000

$y = 1$ to 3

$p = 1$ to 200

wherein R and R_1 are independently selected from the group consisting of hydrogen, alkyl groups having 1 to 6 carbons, 15 phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R_2 is selected from the group consisting of C_1 to C_6 alkyl, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R_3 is methyl, ethyl or propyl; and Z is O, S, NH or NR' wherein R' is phenyl, C_1 to C_4 alkyl or C_1 to C_3 20 alkylphenyl.

DETAILED DESCRIPTION OF THE INVENTION

A. Definitions

By "comprising" herein is meant that additional steps may be taken in the processing which do not substantially change the reaction parameters or the product produced by 25 the reaction. The term comprising encompasses the terms "consisting of" and "consisting essentially of". The term also means that the polymer produced by the reaction process may contain other materials or be mixed with other materials but not so that polymer's bulk properties are 30 changed.

By "siloxane" as used herein is meant an organic derivative of polymeric silicon oxide. Preferably the

siloxane is a dimethylsiloxane derivative containing one alkyl amino substituent.

By "polyolefin" as used herein is meant a polymer derived from a ethylene or a substituted ethylene. These include propylene, styrene, alkyl styrenes, butylene, butadienes, acrylates and the like.

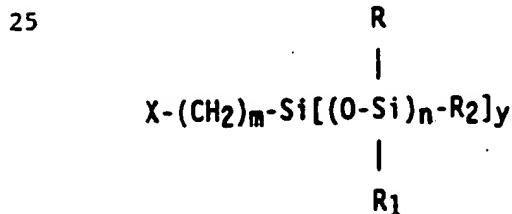
By "reactive group" as used herein is meant a functional group which will react with a corresponding functional group to form a stable compound. Reactive groups encompass alcohols, thiols, primary and secondary amines which will react with carboxylic acids, carboxylic anhydrides, acid chlorides and isocyanates to form esters, amides, imides and ureas or urethanes.

By "terminal" as used herein is meant that the reactive group is at the end or near the end of the hydrocarbon chain or monomeric unit of the polymer. The reactive group can also be located internally or toward the center of the molecule if it is not sterically hindered.

All percentages herein are by weight unless otherwise indicated. The molecular weights of the polymers are determined by a weight average and are based on average molecular weight.

B. The Reactants

1. Siloxanes

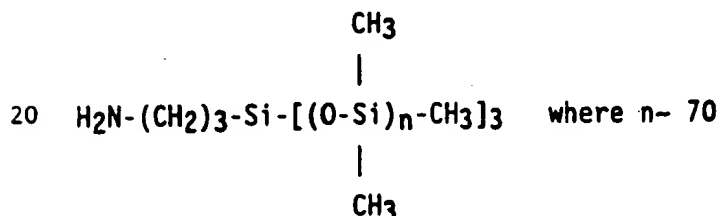


wherein X is selected from the group consisting of NH₂, NHR', OH or SH, and wherein R', R, R₁ and R₂ are independently selected from the group consisting of C₁ to C₆ alkyl, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons, or hydrogen, and m is from 2 to 100 and n is 0 to 1000 and y is from 1 to 3.

The preferred polysiloxanes have average molecular weights in the range of 5000 to 300,000, preferably from 8000 to 200,000, most preferably from 9000 to 40,000.

During the preparation of the polysiloxanes, the molecular weight can be controlled within a general range. There will be some molecules present in the polysiloxanes that have more than one functional group $(CH_2)_nX$. On average the functional groups should be a single or mono-substituted product. More highly substituted polysiloxanes cause the resultant films to form gels, have uneven thickness and limited processability.

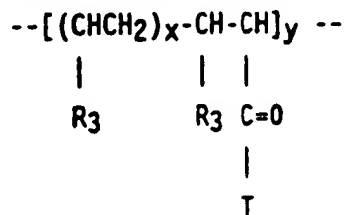
A highly preferred polysiloxane is a primary amino substituted polysiloxane wherein R and R_2 are methyl; X is an amino group linked by a propyl and n is 70. The average molecular weight is 10,000 or 30,000. This is an experimental material available from General Electric (U.S., as products 1159-524 and 1149-165). The compound has the following structure



Other preferred materials are those in which the functional group is an alcohol.

Polyolefins

The polyolefins have the general formula:

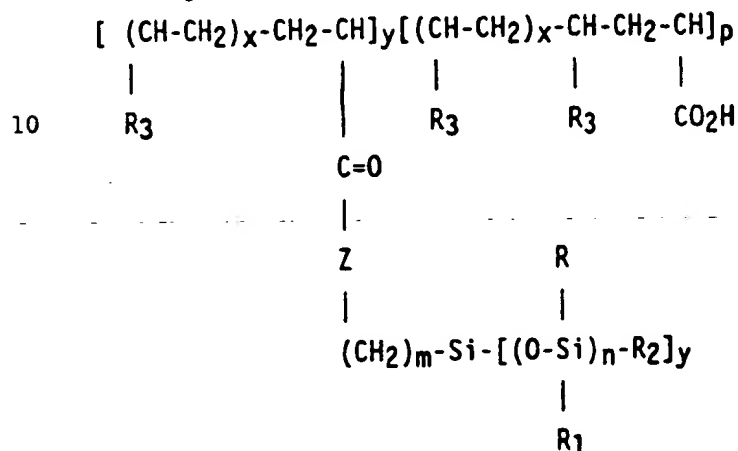


wherein T is OH ; Cl ; an anhydride; isocyanate; or OR_6 wherein R_6 is methyl, ethyl or propyl; and x is 1 to 1000 and y is 2 to 3. The anhydride can be the same as the polyolefin or an alkyl anhydride such as acetyl anhydride, benzoyl anhydride, etc.

The preferred materials are ethylene (acrylic acid) copolymers acid derivatives with a melt index in the range of 3 to 20 gm./10min. These materials are available from Dow Chemical under the Brand name Primacor®. Maleic acid anhydride polymers are also preferred.

The Copolymer

The copolymer is a chemically bonded block copolymer of the general formula



wherein:

$$x = 1 \text{ to } 1000$$

$$m = 2 \text{ to } 100$$

$$n = 0 \text{ to } 1000$$

$$y = 1 \text{ to } 3$$

$$p = 1 \text{ to } 200$$

wherein R and R₁ are independently selected from the group consisting of hydrogen, alkyl groups having 1 to 6 carbons, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R₂ is selected from the group consisting of C₁ to C₆ alkyl, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R₃ is methyl, ethyl or propyl; and Z is O, S, NH or NR' wherein R' is phenyl, C₁ to C₄ alkyl or C₁ to C₃ alkylphenyl.

Process for Making

Polyolefin and polysiloxane are added separately to a twin screw extruder or single screw extruder equipped to heat the materials while mixing and extruding the materials. The ratio of siloxane to olefin ranges from 10:1

to 1:100, preferably the range is from 1:1 to 1:100 ratio is used. This ratio of the two reactants is on a weight basis.

5 The extruder is configured to produce intimate mixing in zone 1 and heating and mixing in the other zones. The preferred extruder is a twin screw extruder. Twin screw extruders are available from a number of companies. The preferred extruder is the Werner and Pfleiderer ZSK70 and ZSK300 (Germany). The extruder is equipped with kneading
10 screws and kneading discs.

The reactants are heated to 150°C to 300°C as they pass through the extruder. No solvent is used in the process. The extruder is vented to remove by-products formed during the reaction process. The mixing speed is
15 from about 50 to about 350 rpm, preferably from about 200 to about 300, and most preferably from about 220 to about 260.

In a preferred process the extruder is divided into 7 zones. The polyolefin is fed into the first zone from a
20 hopper. The polyolefin is heated to from about 150°C to about 225°C to plasticize. The second zone is heated to about the same temperature. This zone consists of a kneading/mixing section (about 1/3) followed by a pumping feeding section. The siloxane polymer is injected at the
25 beginning of the third zone. This is a mixing section. It is heated to about 25°C to 60°C above the prior zones.

The fourth zone is at the same temperature. It is primarily a pumping and reaction zone. The fifth zone has a short kneading section (10% to 20% of its length). This
30 latter section is under a vacuum which allows the by-products to be vented. The last zone is a pumping and discharging zone. The copolymer exits through a die.

The length of the extruder and the screw configurations can be varied as can the reaction temperatures.

35 This process has the advantage of being solventless and thermally activated.

The following examples are illustrative of the invention but are not limiting thereof.

EXAMPLE I

5% GE 1149-165 Compounded with Primacor 3460R

	<u>Twin Screw Compounder</u>	<u>Temperature°C</u>
5	Zone A	200
	Zone B	200
	Zone 1	239
	Zone 2	241
10	Zone 3	239
	Zone 4	239
	Zone 5	239
	Melt Temp	248
	Screw Speed (rpm)	250
15	Resin Feed Rate (rpm)	23
	Die Pressure (psi)	36
	Torque (%)	20
	Vacuum ("Hg)	-25
	Gear Pump Input Pressure (psi)	90
20	Gear Pump Speed (rpm)	13
	Gear Pump Output Pressure (psi)	300-600
	Material Collected (lbs)	20

The extrudate is white and smooth coming out of the die.

GE 1149-165 is an experimental monoamine terminated
 25 polydimethylsiloxane with an average molecular weight of 30,000 grams/ml. Primacor 3460R is a ethylene-acrylic acid copolymer available from Dow Chemical Corporation. It has a melt index of 20 and 9.5% acrylic acid.

The Primacor is fed into the first zone of a twin
 30 screw extruder that has been divided into seven zones. The Primacor is heated to about 200°C to plasticize it. The second zone consists of a kneading/mixing section followed by a pumping feeding section. The polyolefin passes from the first zone into the second zone which is also at 200°C.
 35 The third zone is at a temperature of 239°C and is equipped as a mixing section. The siloxane polymer is injected at

the beginning of this zone. A pumping and reaction zone follows as the fourth zone. This is also held at a temperature of about 240°C. A fifth zone has a short kneading section approximately 10-20% of its length. It is under a vacuum (1 inch of mercury). This allows the by-products to be vented. The last zone is a pumping and discharging zone and it is held at a temperature of about 240°C.

EXAMPLE II

Reactive Extrusion of Primacor 3150 with 5% (wt.)

GE 1149-165 Polydimethylsiloxane

Primacor 3150, ethylene acrylic acid copolymer, 3% acrylic acid, melt index of 11 g./10 min; is introduced into the Werner and Pfleiderer twin screw extruder with 5% by weight GE 1149-165, -30,000 MW amine terminated polydimethylsiloxane. The extruder is equipped as in Example I and these conditions are used.

	<u>Twin Screw Compounder</u>	<u>Temperature°C</u>
	Zone A (C)	200
	Zone B (C)	200
20	Zone 1 (C)	236
	Zone 2 (C)	232
	Zone 3 (C)	238
	Zone 4 (C)	239
	Zone 5 (C)	240
25	Melt Temp (C)	248
	Screw Speed (rpm)	247
	Resin Feed Rate (rpm)	23
	Die Pressure (psi)	40
	Torque (%)	40-42
30	Vacuum ("Hg)	-24
	Gear Pump Input Pressure (psi)	90
	Gear Pump Speed (rpm)	13
	Gear Pump Output Pressure (psi)	300

The material extruded is white, smooth and slightly sticky/oily in feel.

EXAMPLE IIIReactive Extrusion of Primacor 3340 with 5% (wt.)GE 1149-165 Polydimethylsiloxane

Primacor 3340, ethylene acrylic acid copolymer 6.5%
 5 acrylic acid, 9.0 g./10 min. melt index; was introduced
 into a Werner-Pfeiderer twin screw extruder as in Example I
 with 5 weight % GE 1149-165 amine terminated polydimethyl
 siloxane (30,000 MW avg.). The extrusion conditions are
 listed below. A white, smooth material was extruded which
 10 did not feel oily or tacky.

	<u>Twin Screw Compounder</u>	<u>Temperature°C</u>
	Zone A	200
	Zone B	200
	Zone 1	239
15	Zone 2	239
	Zone 3	240
	Zone 4	241
	Zone 5	241
	Melt Temp	249
20	Screw Speed (rpm)	248
	Resin Feed Rate (rpm)	23
	Die Pressure (psi)	40-50
	Torque (%)	40-42
	Vacuum ("Hg)	-24
25	Gear Pump Input Pressure (psi)	90
	Gear Pump Speed (rpm)	13
	Gear Pump Output Pressure (psi)	300

EXAMPLE IV10% GE 1149-165 Compounded With 90% Primacor 3460R

30 Primacor 3460R, an ethylene acrylic copolymer
 available from Dow Chemical is reacted with 10% GE 1149-165
 in a twin screw extruder as in Example I. The following
 conditions are used.

	<u>Twin Screw Compounder</u>	<u>WK 1066-74</u>
	Zone A	200
	Zone B	200
	Zone 1	241
5	Zone 2	240
	Zone 3	241
	Zone 4	240
	Zone 5	240
	Melt Temp	248
10	Screw Speed (rpm)	248
	Resin Feed Rate (rpm)	23
	Die Pressure (psi)	20
	Torque (%)	32
	Vacuum ("Hg)	-25
15	Gear Pump Input Pressure (psi)	90
	Gear Pump Speed (rpm)	25
	Gear Pump Output Pressure (psi)	950

Extrudate was white and smooth coming out of the die.

EXAMPLE V

20 2.5% GE 1149-165 Compounded with 97.5% Primacor 3460R

GE 1149-165 is a mono-amine terminated polydimethylsiloxane with an average molecular weight of 30,000 g/ml. It is reacted with Primacor 3460R as in Example I. The following conditions are used.

	<u>Twin Screw Compounder</u>	<u>Temperature °C</u>
	Zone A	200
	Zone B	200
	Zone 1	240
5	Zone 2	246
	Zone 3	241
	Zone 4	239
	Zone 5	235
	Melt Temp	243
10	Screw Speed (rpm)	250
	Resin Feed Rate (rpm)	23
	Die Pressure (psi)	38
	Torque (%)	20
	Vacuum ("Hg)	-25
15	Gear Pump Input Pressure (psi)	90
	Gear Pump Speed (rpm)	6.5
	Gear Pump Output Pressure (psi)	0-300

An acceptable polymer is made.

Uses:

20 The polymers of this invention are thermoplastic, melt processable, coextrudable into very thin layers and heat sealable to themselves and other compatible polymers. These properties give them a number of uses.

A. Adhesive Release - The siloxane modified polyolefin
 25 polymers can be used alone as adhesive release materials. The polymers are coated onto paper fiber or film to make adhesive release materials. The adhesive and the silicone must be compatible so that the adhesive is not dissolved by the polymer or its adhesive properties reduced by partial
 30 solution or reaction with the polymer. It is important that the silicone does not transfer or contaminate the adhesive.

B. Film and Packaging - The polymer can be extruded or co-extruded with a polyolefin or other polymer to make
 35 films and packages. The copolymer of this invention provides the silicone properties of adhesive release, fast draining, non-drip and water resistant yet it is compatible

with other olefin polymers such as polyethylene. It can be coextruded into very thin layers simultaneously with another layer of polymer to make a permanently affixed silicone film on the polyethylene or other compatible polymer. It can also be blown or cast into a multilayer film or coextruded as a thin layer on a bottle or other package.

The copolymers can be used to make liquid dispensing packages such as those described in U.S. 4,696,416 issued to Muckenfuhs, et al. (1987), and U.S. 5,181,630 issued to McNally (1993). They can also be used to make articles which contain a segment which can be elastically sheared, as, for example, the articles described in U.S. 4,908,247 issued to Baird, et al. (1990).

15 Characterization of the Product

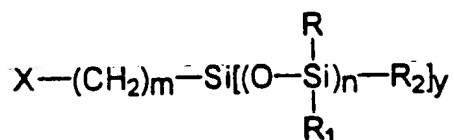
An important property of the material is that the copolymers are chemically bonded. This means that the siloxane will not separate from the polymer. Physical mixtures or ionically bonded copolymers tend to separate on standing. This causes the siloxane to be lost. As it migrates to surface, an oily film forms making the film, package or sheet feel greasy. The siloxane can also migrate into the materials or food wrapped or packaged in the polymer.

25 The polymers formed herein do not suffer this disadvantage. X-ray photoemission spectroscopy shows that the surface of the film is primarily silicone. Transmission electron microscopy confirms that the materials are chemically bonded and not just mixed.

What is claimed is:

1. A process for preparing a siloxane modified polyolefin copolymers comprising reactively extruding organosiloxanes having reactive terminal groups with polyolefins having reactive groups, the molar ratio of the functional groups being from 1:1 to 1:100,000 in a substantially solvent-free environment at a temperature from 150°C to 350°C for not more than 1 hour at 200 to 350 rpm, preferably from 200 to 300 rpm.

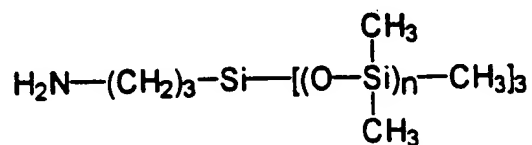
2. A process according to Claim 1 characterized in that the siloxane has the general formula:



wherein X is NH₂, NHR', OH or SH, and wherein R' is phenyl, C₁ to C₄ alkyl or C₁ to C₃ alkylphenyl; R, R₁ and R₂ are independently hydrogen, C₁ to C₆ alkyl, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; and m is from 2 to 100 and n is 0 to 1000 and y is from 1 to 3.

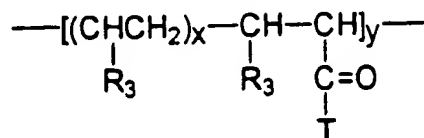
3. A process according to Claim 2 characterized in that the polyolefin is a polymer derived from a ethylene or a substituted ethylene, preferably the polyolefin is a propylene, styrene, alkyl styrene, butylene, butadiene, acrylate or mixture thereof, the process further characterized in that the reactive terminal group is an alcohol, thiol, primary or secondary amine which reacts with carboxylic acid, carboxylic anhydride, maleic anhydride, acid chloride or isocyanate to correspondingly form esters, amides, imides, ureas or urethanes.

4. A process according to Claim 3 characterized in that the polysiloxane has the formula:



wherein n is 70.

5. A process according to Claim 3 wherein the polyolefin has the general formula:

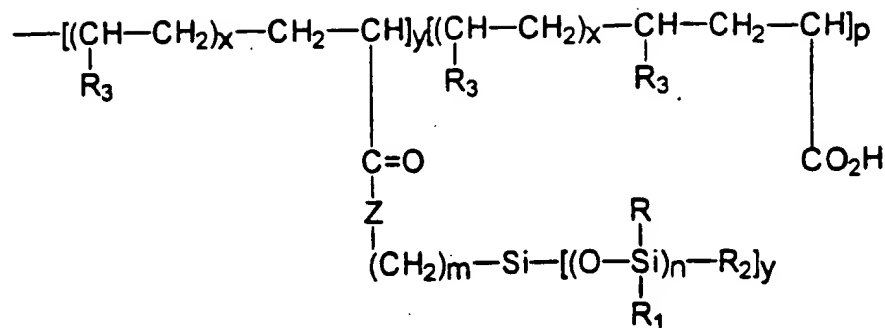


wherein T is OH; Cl; an anhydride; isocyanate; or OR₆ wherein R₆ is methyl, ethyl or propyl; and x is 1 to 1000 and y is 2 to 3, preferably the polyolefin is a polyethylene carboxylic acid derivative with a melt index in the range of 5 to 20 gm./10min.

6. A process for preparing a siloxane modified polyolefin copolymers characterized in that the process comprises reactively extruding organosiloxanes having reactive terminal groups and a viscosity of at least 1000 cps with polyolefins having reactive groups, the molar ratio of the functional groups being from 1:1 to 1:100,000 in a substantially solvent-free environment at a temperature from 150°C to 350°C for not more than 1 hour at 200 to 350 rpm, wherein the extruder is divided into 7 zones comprising the following steps:

- (1) polyolefin is fed into the first zone from a hopper and heated from 150°C to 225°C to plasticize it;
- (2) polyolefin is heated in a second zone from 150°C to 225°C with kneading/mixing;
- (3) siloxane polymer is injected at the beginning of a third zone where it is mixed and heated from 175°C to 285°C;
- (4) the mixture is pumped through a fourth zone while it is heated; and
- (5) the mixture is kneaded in a fifth zone which is under a vacuum to vent the by-products;
- (6) the copolymer is then pumped and discharged through a die.

7. A siloxane polyolefin copolymer characterized in that it has the formula:



wherein:

$x = 1$ to 1000

$m = 2$ to 100

$n = 0$ to 1000

$y = 1$ to 3

$p = 1$ to 200

wherein R , R_1 and R_2 are independently hydrogen, alkyl groups having 1 to 6 carbons, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R_2 is C_1 to C_6 alkyl, phenyl, benzyl or alkylphenyl having from 6 to 12 carbons; R_3 is methyl, ethyl or propyl; and Z is O, S, NH or NR' wherein R' is phenyl, C_1 to C_4 alkyl or C_1 to C_3 alkylphenyl; preferably Z is NH, R^1 and R^2 are methyl and n is 70.

8. A copolymer according to any of Claims 1-5 characterized in that the polysiloxane fragment has an average molecular weight in the range of 5000 to 300,000, more preferably from 8000 to 200,000, more preferably still from 10,000 to 30,000.

9. An adhesive releasable material made from a siloxane modified copolymer according to any of Claims 7 or 8.

10. A liquid dispensing package made from a siloxane modified copolymer according to any of Claims 7 or 8.

11. A film made from a siloxane modified copolymer according to any of Claims 7 or 8.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08G77/42 C08L83/06 C08L83/08 C08L23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 235 728 (BAYER AG.) 9 September 1987 see claims 1-4 see page 4, line 1 - line 4 see page 4, line 16 - line 17 ---	1-5
X	US,A,4 978 436 (PETER Y. KELLY) 18 December 1990 see claims 1-5 see column 1, line 5 - line 10 see column 2, line 58 - line 68 see column 3, line 16 - line 27 see column 4, line 8 - line 31 --- -/--	1-5

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "P" document published prior to the international filing date but later than the priority date claimed

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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

10 November 1994

Date of mailing of the international search report

28. 11. 94

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Depijper, R

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,X	EP,A,0 559 515 (RHÔNE-POULENC CHIMIE) 8 September 1993 see claim 1 see page 2, line 55 - page 3, line 2 see page 3, line 12 - line 45 see page 4, line 10 - line 13 see page 5, line 38 - line 47 ---	1-5
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